THESIS.

BY

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THE EQUIVALENT CONDUCTANCE OF SOLUTIONS OF PICRIC ACID.

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Introduction.

Picric acid possesses the property, which is rare among strong electrolytes, of having a convenient distribution ratio between water and certain organic solvents such as benzene, chloroform, etc. Because of this property, picric acid offers peculiar advantages for studying the well known deviations of strong electrolytes from the law of mass action, for; by means of distribution experiments, the activities of picric acid in various aqueous solutions may be compared.

In order to interpret the results of such distribution experiments, it is necessary to know the degree of ionization of picric acid in aqueous solutions.

At least three series[1] of determinations of the equivalent conductance of picric acid have been published, but the results are not concordant; and therefore, the degree of ionization cannot be calculated with any degree of certainty.

The object of the present investigation was to redetermine the conductance of picric acid solutions in order to obtain satisfactory data from which the degrees of ionization of its solutions might be calculated.

1. Ostwald, Z. Ph. Chem. 1, 74. Rothmann and Drucker, Z. Ph. Chem. 46, 827. H. Gorke, Z. Ph. Chem. 61, 495.

Outline of Method.

Determination of Conductance.

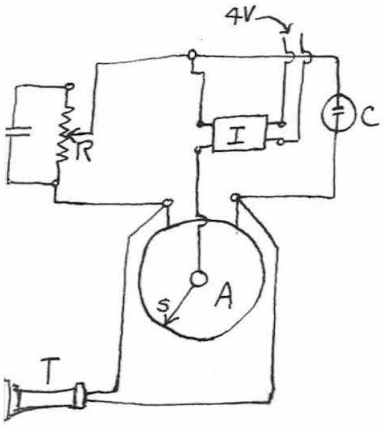


Fig. (1)

The usual Wheatstone Bridge arrangement as shown in fig. (1) was used to measure the conductance. A is a Kohlrausch slide wire bridge. Across its terminals is placed a telephone receiver T, while in series with it are placed the conductivity cell C, and the variable resistance R. I is an induction coil, the secondary of which is connected to the slider S and the heavy copper lead connecting C and R. B is a small variable air condenser which may be employed to balance the capacity of the cell C, thus giving a more distinct minimum sound point in the telephone when the system is balanced. The cell C was kept in a thermostat at a temperature of $25 \pm .02^{\circ}$ C.

In order to obtain greater silence during the measurements, the buzzer was placed in an adjoining room under a bell jar, and suspended from the cork in such a way that it did not touch the sides. The jar was placed on a heavy felt pad. With this arrangement very little sound was audible even in the room where the buzzer was.

The cells employed were of the pipette design as shown in fig. (2). Two such cells were used; one, with electrodes about 15mm apart for concentrated solutions, the other, with electrodes about 8mm apart for the more dilute solutions.

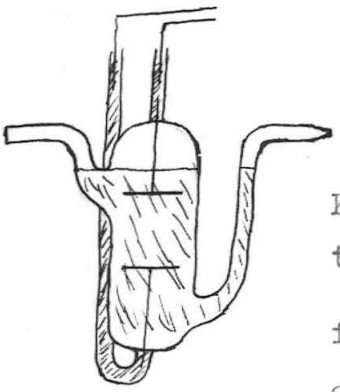


Fig. (2)

The cell constants of both these cells were obtained by measuring the conductance of N/50 KCl solution whose conductance[1] was taken as $2.768 \ 10^{-3}$. The constants for these two cells were found to be 0.5172 and 0.2630 respectively.

Calibration of Slide Wire Bridge.

The following method proposed by Strouhal and Barus[1] was used for calibrating the slide wire bridge.

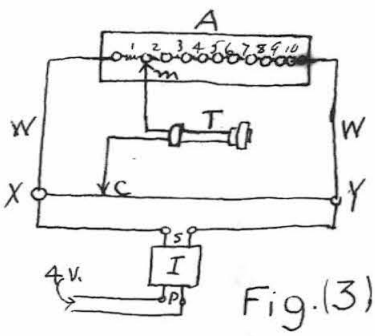


Fig. (3)

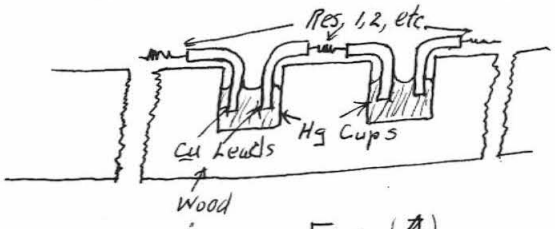


Fig. (4)

1. Findlay, Practical Physical Chemistry.

In a strip of wood A, of about 2inches by 4inches by 3feet, eleven holes, 1 inch deep and 3/4inch in diameter were bored and partly filled with mercury, fig. (4). These cups were connected by means of 10 approximately equal resistances of "Ideal" wire. To each end of each length of resistance wire was soldered a heavy copper lead. This lead dipped into a mercury cup. Each resistance was about 1/10 the resistance of the slide wire bridge XY. The ends of all copper wires dipping into mercury cups were amalgamated. The arrangement is shown in fig. (3) and fig. (4).

The lead M, from the telephone receiver was placed in cup#2 and the point of minimum sound determined.

Then $\frac{XC}{XY} = \frac{R_1}{\Sigma R}$ where R_1 is the resistance of resistance 1 and ΣR the sum of the resistances of the ten wires, (see fig. 3).

Resistances 1 and 2 were then interchanged and the point of minimum sound again determined; then $\frac{XC'}{XY} = \frac{R_2}{\Sigma R}$. The lead was moved to cup#3; then when the system was balanced, $\frac{XC''}{XY} = \frac{R_1 + R_2}{\Sigma R}$ and $\frac{CC''}{XY} = \frac{R_1}{\Sigma R}$. Hence a distance CC'' is obtained whose resistance corresponds to resistance I, i.e. the resistance of CC'' equals that of XC.

By replacing in this manner each of the resistances by resistance 1, ten distances on the slide wire bridge of exactly the same resistance are obtained. If these distances are of equal length no calibration correction is applied. If not, the corrections may be readily calculated.

The bridge calibrated as above, was found to be accurate to 0.02 percent between readings of 40 and 60 cm. All subsequent readings were limited to this range.

Conductivity Water.

The conductivity water used was from a conductivity still and always had a conductance less than 3×10^{-6} reciprocal ohms. The average value for the water used was about 1.5×10^{-6} reciprocal ohms. All bottles, flasks, burettes, etc., which came in direct contact with the conductivity water were well cleaned and steamed before using.

Purification of Picric Acid.

It may be that the discrepancies occuring in the results of previous workers were due to impurities in the picric acid. Hence in this determination particular care was taken to secure pure acid. A sample of Merck's picric acid was crystallized three times from water and twice from alcohol.

Hereafter this is called sample A. Next some of Baker's C.P. picric acid was used. One lot, sample B, was crystallized twice from water, once from alcohol, and once again from water. Another lot, sample C, was crystallized but twice from water.

Analysis of Solutions.

In order to determine the concentration of the picric acid solutions, the following method was used. A nearly saturated solution of acid was made at room temperature, and its concentration determined by titrating against a standard solution of barium hydroxide, using phenolphtalein as indicator.[1] The density and the conductance of this solution were then found. The other solutions of acid were made from this one by adding a known weight of water to a known weight of solution, it being assumed that the volumes were additive.

The barium hydroxide solution was kept carbon dioxide free by an arrangment as shown in fig.(5). ~~In this manner~~.

1. Rothmann and Ducker used same method to determine the concentrations.

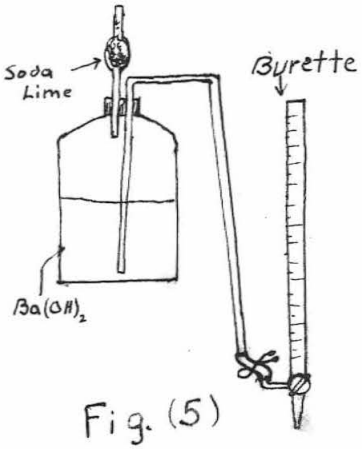


Fig. (5)

In this manner the solution was kept fairly constant in strength. The barium hydroxide was frequently titrated against standard HCl, which had been standardized with Kahlbaum's sodium carbonate "Zur Analyses".

Outline of Run.

The actual measuring of the conductance was done at night in order to avoid the disturbance of noises about the building. A nearly saturated solution of acid was made by allowing an excess of solid acid to stand in contact with conductivity water. This was then hastily filtered, and placed in a glass-stoppered flask. Its concentration, density and conductance were then determined.

The more dilute solutions were made by adding water to a known weight of this solution in small conical flasks, and then accurately determining the weight of water added. The small flasks were well steamed amd kept covered with small watch glasses at all times.

The cell was carefully rinsed out three or four times with each solution before its conductance was determined. Three separate settings of the bridge were obtained for the solution, and then the cell was refilled with a fresh lot of the same solution.

The six values thus obtained for the equivalent conductance checked to about 0.05 percent for the concentrated solutions, and about 0.7 percent for the more dilute solutions.[2] The average of these values is recorded in Table 1.

Table 1.

Sample A. C[1]	Λ	Sample B. C #1	Λ	C #2	Λ	Sample C. C	Λ
.03224	340.6	.02248	349.8	.02248	350.1	.01773	354.6
.02409	346.1	.01210	360.4	.01031	360.3		
.01584	352.7	.009385	361.1	.006813	364.9		
.01094	359.0	.005022	367.4	.002915	370.3		
.009804	359.6	.002830	370.7				
.008621	359.8	.001069	376.0				
.005934	365.6	.000845	384.5?				
.003509	369.1						

1. Thruout this paper all concentrations are expressed as mols per litre.

The above results were plotted as shown in Graph#1. The logarithm of $\frac{1}{C}$ is plotted against Λ. One curve each for Merck's and Baker's acid is shown, and a resulting final curve as shown. Graph#2 shows the final curve and also curves representing the results of previous workers.

1.

2. The water correction was neglected all thru the present investigation.

From this final curve the values at several round concentrations were taken. These are given in Table II.

Table II.

.03	.02	.015	.01	.0075	.005	.003	.002	.001
343.9	350.5	354.5	360.3	363.4	367.0	370.3	372.6	376.0

Table III. below gives results of previous investigators and present results in condensed form, the values being taken from plotted graphs.

Table III.

C	Capra	Gorke	Ostwald	Rothmann and Ducker
.03	343.9	342.8	340.5	340.7
.02	350.5	350.5	348.0	346.7
.01	360.3	360.3	360.3	355.2
.005	367.0	367.6	370.4	361.0
.002	372.6	374.0	379.8	366.7
.001	376.0	377.1	384.1	370.2

The Equivalent Conductance at Infinite Dilution.

The data obtained in this investigation was used in determining the equivalent conductance at infinite dilution (Λ_o) for picric acid. The graphic method of A. A. Noyes[1] was used. This consists in plotting values of $\frac{1}{\Lambda}$ against $(C\Lambda)^{n-1}$, substituting different values for N until the plotted points lie on an approximately straight line.

I. Noyes + Falk, (J. Am. Chem. Soc.) 24, 462 (1912)

A fairly straight line was obtained when N=1.55 was employed, (Graph #3). On extrapolating this line to zero concentration the value 383[2] was obtained as the Λ_o value for picric acid.

There is considerable uncertainty regarding the value to be used for the equivalent conductance of the hydrogen ion at infinite dilution at 25° C. Kendall,[1] who has made a careful study of this question uses the value 347.2. This gives 36 as the equivalent conductance of the picrate ion. Noyes and Falk,[4] in their critical compilation of data, give 350 as the value for the hydrogen ion; this gives 33 for the picrate ion. In order to obtain further information upon this point, the conductance of solutions of sodium picrate was determined.

Conductance of Sodium Picrate.

The sodium picrate was made by adding a slight excess of sodium carbonate to a boiling, saturated, picric acid solution and evaporating until crystals appeared. The salt

1. Kendall (J. Am. Soc.) 101, 1283 (1912), (J. Am. Chem. Soc.) 39, 16 (1917)
2. H. Gorke, (Z. Ph. Chem.) 61, 495, obtains 384 for Λ_o.
3. Sibberrad and Phillips, (Chem. Soc. Trans.) 93, 474 (1908).
4. Noyes and Falk, (J. Am. Chem. Soc.) 34, 479 (1908).

was then recrystallized three times from water. Since there seems to be a difference of opinion among investigators[3] as to whether this salt is anhydrous or not, it was heated for about four hours at 150°- 170° C in order to obtain the anhydrous salt. A fairly concentrated solution was then made up by weight, special precautions being observed to protect the salt from moisture until its weight had been determined.

Following are the results obtained and which are plotted in Graph #4.

Table IV.

C	.0364	.0167	.0107	.00641	.00232
Λ	71.2	73.2	75.4	76.8	79.0

From the smooth curve in Graph #4, values were taken for Graph #5 where $\frac{1}{\Lambda}$ was plotted against $(C\Lambda)^{n-1}$. A straight line was obtained when N = 1.45. On extrapolating to zero concentration the value 83.5[1] was obtained for the Λ_o value of sodium picrate. Then taking 51.2 as the equivalent conductance of the sodium ion[2], the value 32.2 is obtained for the picrate ion.

1. Gorke got 81.8 for this Λ_o value.
2. Noyes and Falk, as cited.
3. See Note 3 of preceeding page.

Summary.

That the picric acid obtained from different sources gave practically the same results indicates that the acid used was pure. The results of this investigation check H. Gorke's work and not the other two investigators. If Noyes value for Λ_H of 350 is used, $\Lambda_{picrate} = 33$. If Kendalls' value of Λ_H, 347, is used, $\Lambda_{picrate} = 36$. From value of sodium picrate found, $\Lambda_{picrate} = 83.5 - 51.2 = 32.3$. This checks value of Λ_H given by Noyes and Falk better than it does that given by Kendall.

Following is a table giving γ, the degree of ionization of picric acid at several concentrations.

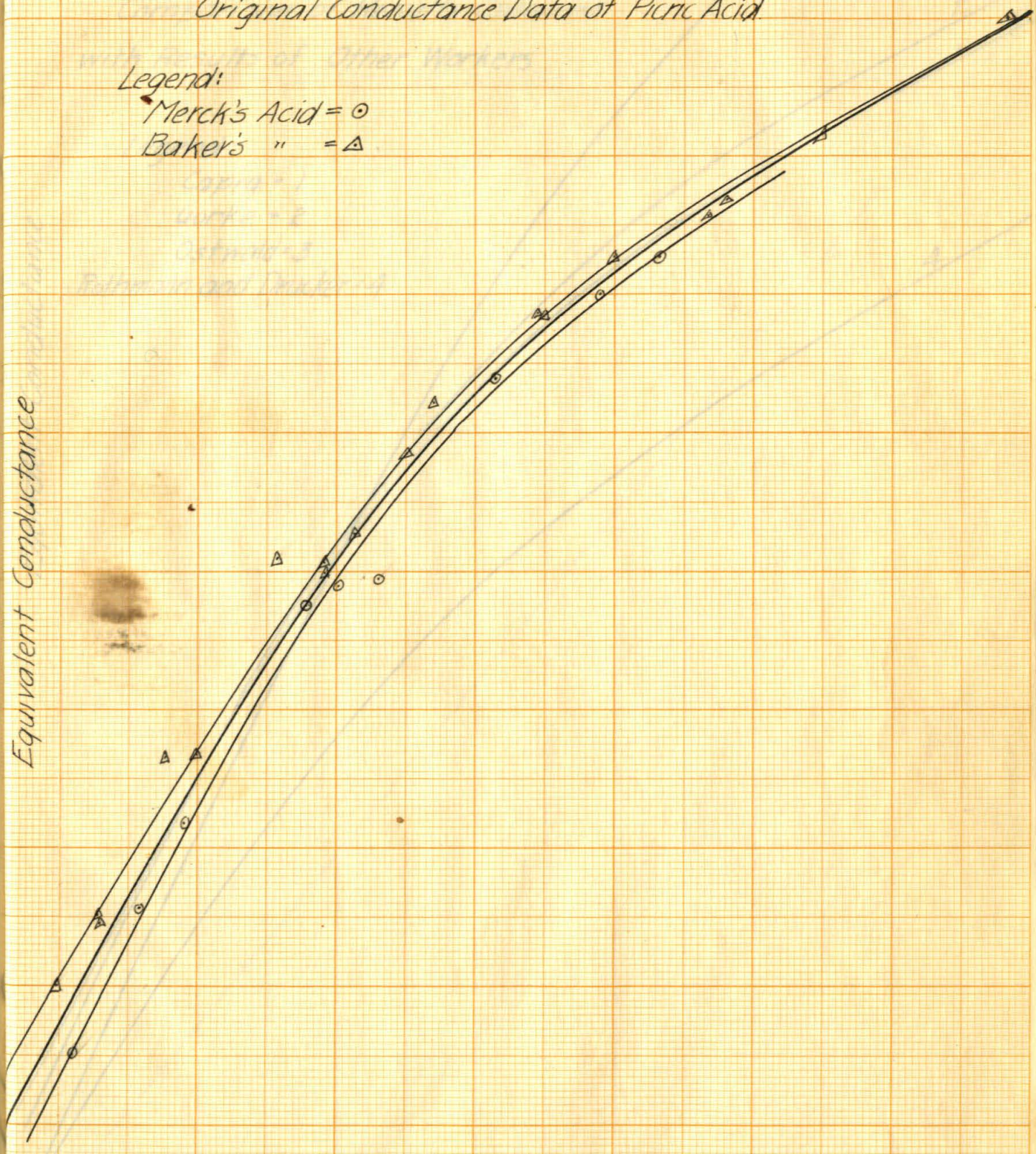
Table V.

C	.03	.02	.015	.01	.0075	.005	.003	.002	.001
γ	.897	.9165	.926	.941	.949	.958	.968	.973	.982

Graph #1

Original Conductance Data of Picric Acid

Legend:
Merck's Acid = ⊙
Baker's " = △

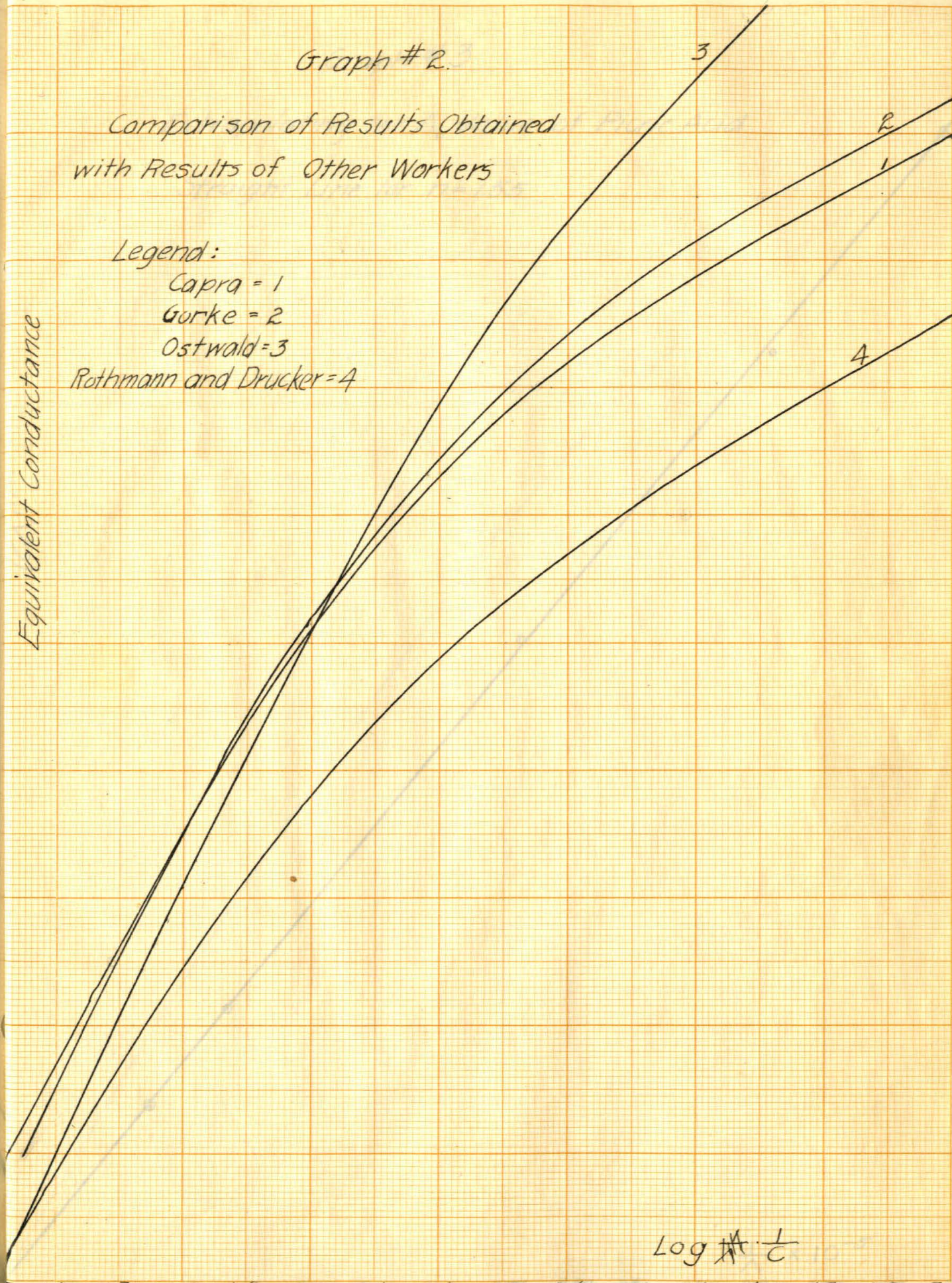


Graph #2.

Comparison of Results Obtained with Results of Other Workers

Legend:

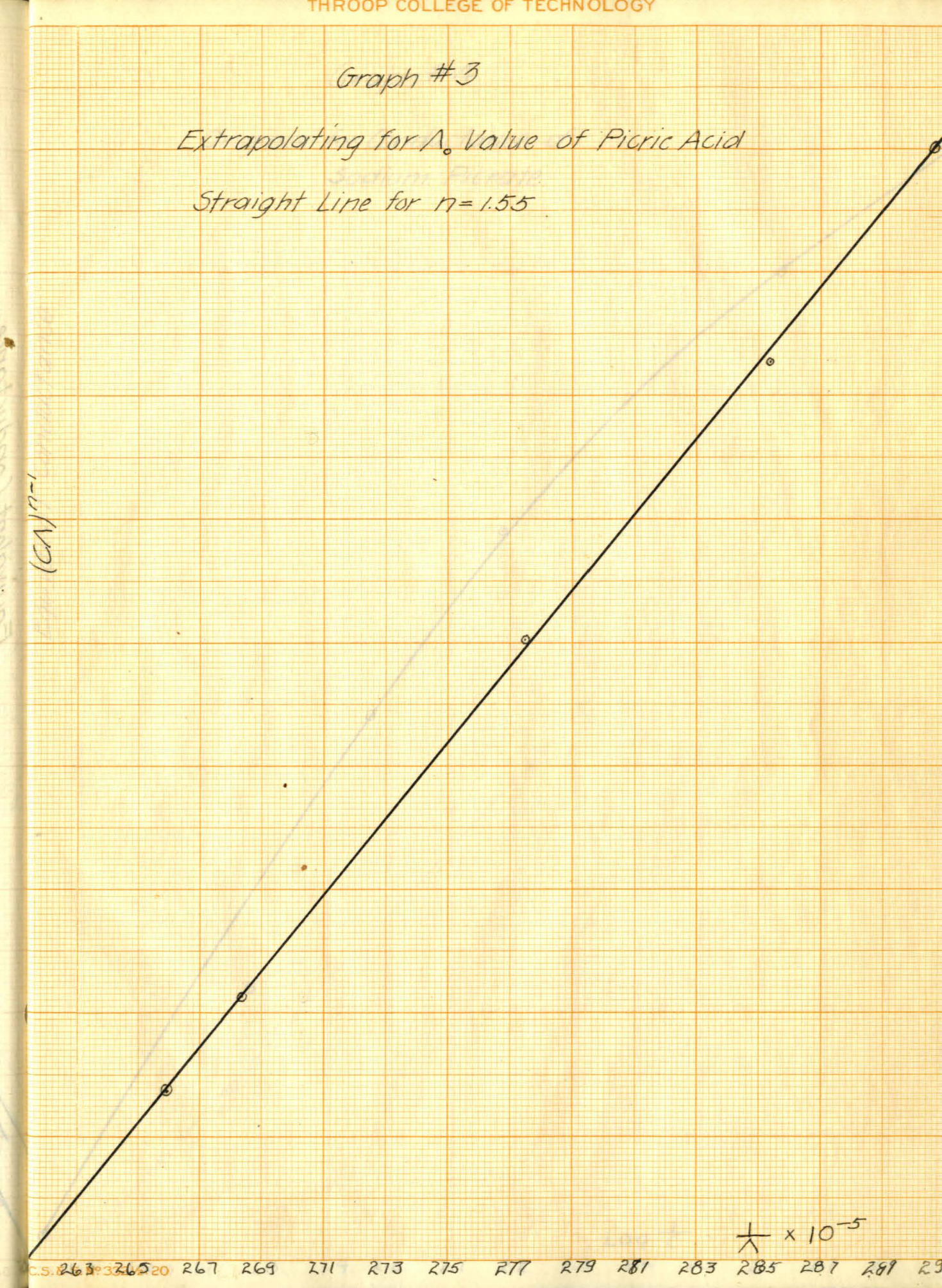
Capra = 1
Gorke = 2
Ostwald = 3
Rothmann and Drucker = 4



Graph #3

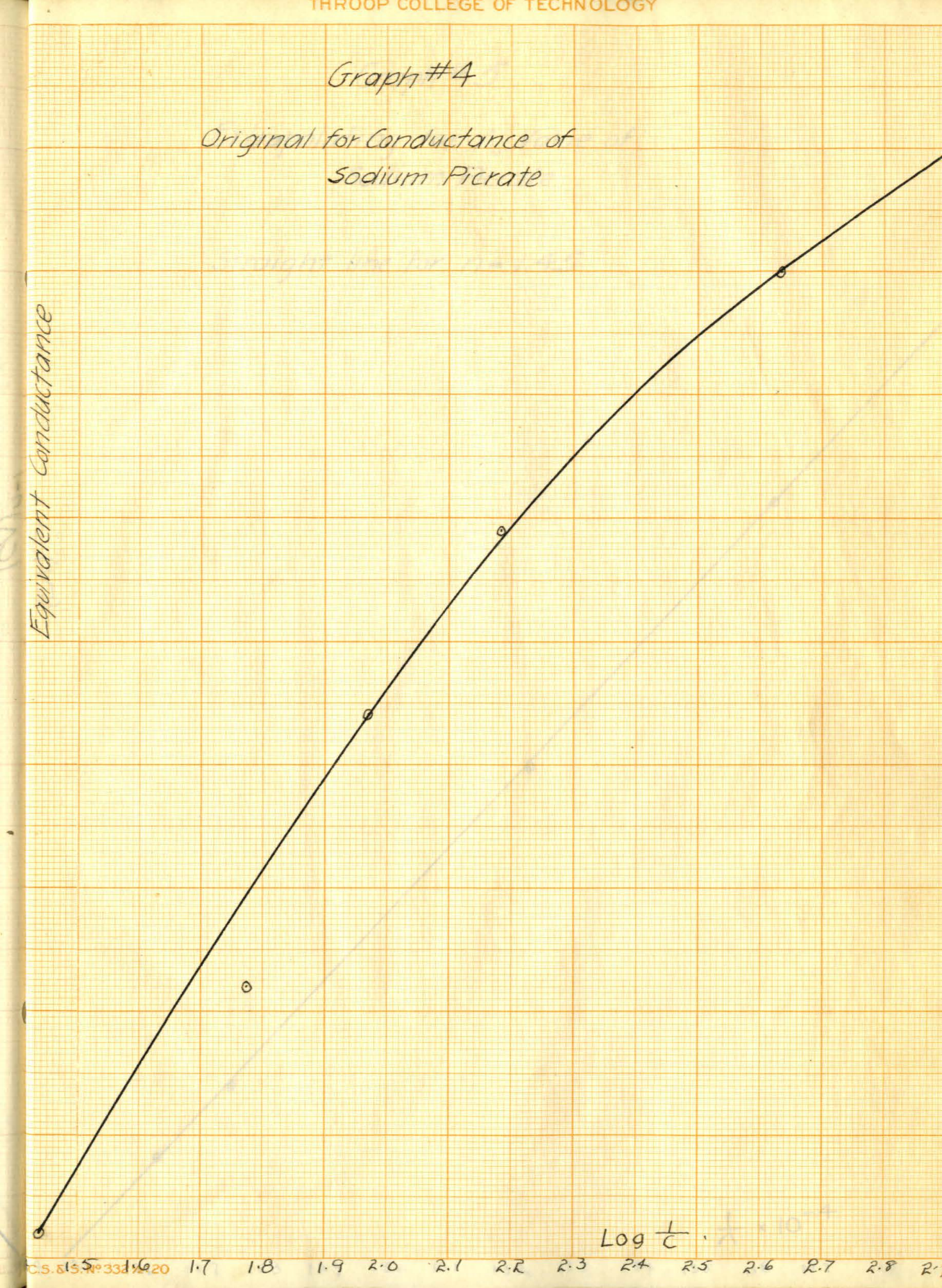
Extrapolating for Λ_o Value of Picric Acid

Straight Line for $n = 1.55$



Graph #4

Original for Conductance of Sodium Picrate



Graph #5

Extrapolating for Λ_0 Value of Sodium Picrate

Straight line for $n = 1.45$